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ARTICLE

Superbase ionic liquids for effective cellulose processing from dissolution to carbonisation.

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A range of superbase derived ionic liquids (SILs) was synthesised and characterised. Their ability to dissolve cellulose and the characteristics of the produced fibres were correlated to their specific structural and solvent properties. 17 ionic liquids (ILs) (including 9 novel) were analysed and six ILs were selected to produce fibres: 1-ethyl-3-methylimidazolium acetate [C_2C_1im][OAc], 1-ethyl-3-methylimidazolium diethyl phosphate [C_2C_1im][DEP] and the SILs 1-ethyl-1,8-diazabicyclo[5.4.0]undec-7-enium diethylphosphate [DBUEt][DEP], 1,8-diazabicyclo[5.4.0]undec-7-enium acetate [DBUH][OAc], 1,5-diazabicyclo[4.3.0]non-5-enium acetate [DBNH][OAc] and 1-ethyl-1,5-diazabicyclo[4.3.0]non-5-enium diethylphsophate [DBNEt][DEP]. The mechanical properties of these fibres were investigated. The obtained fibres were then carbonised to explore possible application as carbon fibre precursors. The fibres obtained using a mixture of 1,5-diazabicyclo[4.3.0]non-5-enium based SILs with acetate and hexanoate anions (9:1), [DBNH][OAc][Hex], showed a promising combination of strength, stiffness and strain at failure values for applications in textiles and fibre reinforcement in renewable composites. Using Raman spectroscopy it is demonstrated that these fibres exhibit a relatively high degree of structural order, with fewer defects than the other materials. On the other hand, analogous fibres based on imidazolium cation with acetate and hexanoate anions (9:1), [C_2C_1im][OAc][Hex] showed a decline in the quality of the produced fibres compared to the fibres produced from [C_2C_1im][OAc], [C_2C_1im][DEP] or [DBNH][OAc][Hex].

Introduction

Today's society is highly dependent on petroleum based, non-renewable, polymers. To decrease the environmental impact of these materials large-scale utilisation of naturally occurring, abundantly available, polymers such as cellulose, chitin, starch and keratin needs to be developed. The viscose process is the most common way to manufacture cellulose fibres. Viscose rayon – the first commercially available synthetic fibre was developed around 1910 and used as a reinforcement material for tyres and, subsequently by the 1920s, other mechanically important rubber goods such as drive belts, conveyors and hoses.[1] However, the manufacture of viscose fibres is a complex, multistep process that involves the use of very aggressive chemicals, which produces a great deal of waste and requires large volumes of fresh water.[2] The viscose process is also known to depolymerise cellulose.[3] Nylon fibres, first commercialised in the late 1930s, and consequent development and commercialisation of polyester fibres in the 1950s[4] defined the beginning of the development and commercialisation of major man-made fibres.[5] In the early 1970s, a single stage spinning and drawing process for nylon fibres was commercialised,[4] petroleum based synthetic polymer fibres were proven to be more economically feasible than cellulose fibres produced via the viscose process. These approaches resulted in polyester fibre becoming the world's dominant fibre since 2007,[6] scaling down of cellulose fibre production and growing production of synthetic fibres, which accounted for 82% of worldwide fibre production by 2014.[7] This trend has not changed with the novel solvents for cellulose that have been developed since the 1970s to replace the environmentally harmful CS_2 solvent in the viscose process. These solvents included LiCl/N,N-dimethylacetamide systems,[8,9] DMSO/paraformaldehyde[10] and N-methylmorpholine-N-oxide (NNMO). The Lyocell (NNMO) process offered some advantages in comparison with other common processes for cellulose manufacture such as a low number of technological steps, no derivatization, good solvent recovery and significantly lower environmental hazard. However, disadvantages and limitations of the Lyocell process are the poor thermal stability of NNMO and its predisposition to side reactions and by-product formation.[11]

At the same time synthetic polymers such as poly(acrylonitrile) (PAN) supplanted cellulose as the main precursor material for controlled pyrolysis for the production of commercial carbon

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fibres.[12] However, the use of toxic solvents in the production of PAN and the emission of waste gases in the manufacturing process of carbon fibres made from it have raised environmental concerns.[13]

Regenerated cellulose has long been considered to be a potentially renewable precursor material to manufacture carbon fibres. Some of the first carbon fibres to be manufactured from cellulose were obtained in the 1950s.[14,15] Despite comparatively poor yield on carbonization, cellulose fibres are competitive as a carbon fibre precursors with respect to thermal conductivity, high purity and mechanical flexibility.[16] Improvement of the carbon yield and mechanical properties of obtained carbon fibres through controlling the cellulose fibres' morphology and optimising processing conditions have offered the main scope for research in this area over the last decade.[16–19]

To overcome the economic and environmental issues of the processing of cellulose, an environmentally benign and low energy method to manufacture high performance natural polymer fibres using solvents known as ionic liquids (ILs) has been developed.[20] However, most ILs are quite expensive and have some other drawbacks limiting their application as cellulose solvents, such as the fact that they can react with cellulose, forming a side product.[21–23] Some work has been undertaken to optimise the existing IL technology and the possibility of IL recovery and recycling by reducing the rate of adduct accumulation when dissolving cellulose in carboxylate ILs by incorporation of small mole fractions of a protic co-solvent.[24] Another promising work included a study of "greener" and "cheaper" morpholinium-based ILs capable of producing highly concentrated cellulose solutions at 80-120 °C and films; the production of fibres from these ILs has not yet been possible.[25–27] Recently, distillable SILs have been developed and used for cellulose dissolution and the production of high performance cellulose fibres. A new process employing a superbase derived acetate IL, the fibres from which are called IONCELL-F, has been developed.[28–30] The ionic liquid 1,5-diazabicyclo[4.3.0]non-5-enium acetate [DBNH][OAc] allowed the production of highly oriented cellulose fibres with superior tenacity, exceeding that of commercial viscose and NMMO-based Lyocell fibers.[28] While [DBNH][OAc] can be recovered from the water by means of distillation,[31] its low thermal stability can affect the cellulose dissolution and spinning processes, which are conducted at elevated temperatures of 60-90 ^{o}C.[29]

Our research is focused on exploring further the potential of SILs, synthesis of novel cellulose dissolving ILs and the development of sustainable and high performance fibres for use as textiles and potential carbon fibre precursors.

Table 1. Thermal properties of the studied SILs, cellulose solubility and cellulose DP_w after dissolution and precipitation with them.

Ionic liquid	T_{melt}	T_{onset} °C	Maximum cellulose solubility, wt%	Cellulose DP_w (±5)
$[C_2C_1im][OAc]$	RT liquid	215	35.2	231
$[C_2C_1im][DEP]$	RT liquid	260	23.0	240
[DBUEt][DEP]*	RT liquid	246	23.0	246
[DBUH][OAc]	56 °C	178	22.5	245
[DBNH][OAc]	61°C	182	22.0	230
[DBNEt][DEP]*	RT liquid	207	21.9	244
$[C_2C_1im][Hex]$	RT liquid	223	16.1	-
[DBNMe][DMP]	RT liquid	266	5.5	-
[DBNH][But]*	RT liquid	-	5.3	-
[TMGH][OAc]	98°C	150	5.1 (110 °C)	-
[DBUH][Prop]	RT liquid	166	4.3	-
[DBNEt][OAc]*	RT liquid	183	2.1	-
[DBNH][Hex]*	RT liquid	171	0.8	-
[DBUH][Hex]*	RT liquid	200	0.7	-
[TBDH][OAc]*	157 °C	235	solid until 157 °C	-

* newly reported SILs; - not determined

We studied the thermal stabilities of our SILs by TGA and compared these to imidazolium based ILs with corresponding anions. Fibres were spun from the solutions of SILs and imidazolium based analogues under similar conditions and their properties were compared. The obtained information helped to identify the most promising ILs for the production of cellulose fibres on an industrial scale. We identified the potential of these ILs to produce stable spinning solutions, and characterised their mechanical properties. Following this we processed them into carbon fibres. Post-carbonisation we

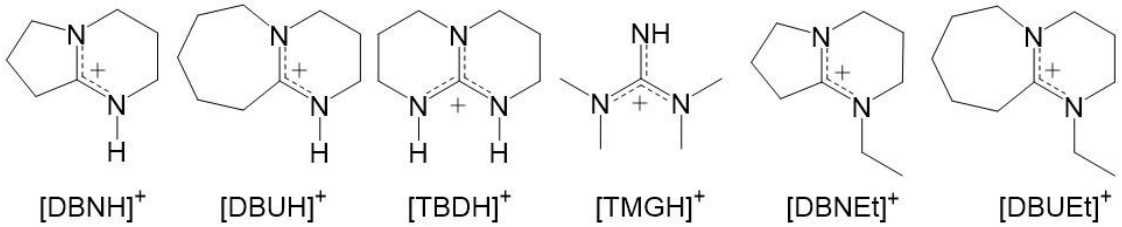

Fig. 1 Superbase derived cations used in this study.

investigated their microstructures using Raman spectroscopy. Progress has been made on the possibility to improve currently applied industrial processes by substituting common solvents with SILs for cellulose fibre processing, and subsequent carbonisation. The advantages and possible drawbacks of our materials choices are also discussed.

Results and discussion

Cellulose solubility

Among the studied SILs, preference was given to ones that are liquid at room temperature, exhibit a good thermal stability and a high cellulose solubility. Cations of the studied SILs are presented in Fig. 1. Additionally, 1-ethyl-3-methylimidazolium acetate ($[C_2C_1im][OAc]$) and 1-ethyl-3-methylimidazolium diethylphosphate ($[C_2C_1im][DEP]$) were studied to compare the performance of SILs against imidazolium based ILs.

$[C_2C_1im][OAc]$ is a known cellulose solvent which is reported to be able to produce a spinnable cellulose solution with up to 15.8% cellulose at 85 °C.[32] Promising results on low energy solubilisation of microcrystalline cellulose (up to 10 wt% in under 1 h in the temperature range 45 – 65 °C) were obtained for $[C_2C_1im]^+$-based ILs with dimethyl phosphate, methyl methylphosphonate and methyl phosphonate anions.[33] Recent studies showed that $[C_2C_1im][DEP]$ is a promising cellulose solvent[34] and allows the production of solutions with concentrations of cellulose in the range 12-14% (at 100 °C)[34] and fibres with good mechanical properties.[35] Therefore it is of interest to study the replacement of the acetate anion with phosphate-based ones and its influence on cellulose reactivity and formation of the side products.

It is known that cellulose solubility is mainly determined by the structure of the anion of the IL, with some influence of its cation.[36] Some acetate SILs have been already synthesised and proven to be effective and easily recycled cellulose solvents for manufacturing of high-performance fibres.[29,30] 15 and 17 % cellulose solutions in [DBNH][OAc] were spun (Ioncell-F process) and the obtained fibres showed high tenacities (above 50 cN/tex) and high initial modulus of up to 34 GPa which is comparable to the highest reported values for NMMO Lyocell fibres of 61 cN/tex and 29.3 GPa, respectively.[29] It was also reported, without quantification however, that acetates and propionates of the bases studied in this work are capable to dissolve cellulose: 1-ethyl-3-methyl imidazolium (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,1,3,3-tetramethylguanidine (TMG).[33] Furthermore, high cellulose solubility was reported in other work for propionate SILS with $[DBNH]^-$, $[DBUH]^-$ and $[TMGH]^-$ cations in range of 15-18 wt%.[37] Additionally a few TMG-based SILs were studied, with only carboxylic TMG-based SILs being found to be cellulose dissolving and able to rapidly dissolve microcrystalline cellulose (5 %, 18h, 100 °C) as well as being “distillable” to over 99% of purity and over 99% yield.[38] [TMGH][OAc] requires higher processing temperatures compared to NMMO-H_2O, $[C_2C_1im][OAc]$ or [DBNH][OAc] solutions and the obtained fibres were reported to be of poor quality.[39] Separately similar behaviour of cellulose dissolution (without quantification of cellulose solubility) in 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH][Prop]) and N-methyl-1,5-diazabicyclo[4.3.0]non-5-enium dimethyl phosphate ([DBNMe][DMP]) with $[C_2C_1im][OAc]$/water mixtures was reported.[40] Similarly the potential of the pretreatment of cellulose for hydrolysis in [DBNH][OAC] and [TMGH][OAc] in comparison to $[C_2C_1im][OAc]$ was investigated, concluding no difference in enzyme compatibility.[41] To the authors’ knowledge the mechanical properties of fibres obtained using [DBNH][OAc] have not been considered to date in relation to their applicability for carbon fibres production.

We decided to extend the research into the promising SILs based on DBN, DBU, TMG superbases and also to synthesise novel SIL based on the 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) superbase.

We hypothesised that the hydrophilic cellulose fibrils could be aligned with long chain carboxylic anions to produce better structured highly oriented fibres. This hypothesis was explored by synthesising and application of propanoate ([Prop]-), and novel butanoate ([But]-) and hexanoate ([Hex]-) SILs with DBU and DBN-based cations.

Out of six studied acetate SILs studied here, only [DBNH][OAc] and [DBUH][OAc] were able to dissolve cellulose in amounts suitable for producing cellulose solutions of concentrations substantially higher than 5 wt% at 80 °C (Table 1). Therefore, the SILs with $[DBNH]^+$ and $[DBUH]^+$ cations were chosen for further study.

Data in Table 1 also show that the solubility of cellulose decreases with the elongation of the ~~S~~IL’s anion chain length. Thus, $[C_2C_1im][Hex]$ was much less efficient in cellulose dissolution than $[C_2C_1im][OAc]$. The replacement of the acetate anion with propanoate, butanoate or hexanoate anions resulted in SILs which were unable to dissolve cellulose at concentrations that allow the spinning of fibres.

However, when these anions were replaced with diethylphosphate, the cellulose dissolution ability of the SILs was ~~even~~ better than for the corresponding acetate SILs. This resulted in the following trend:

[DBNEt][DEP]>[DBNH][OAc]>>[DBNEt][OAc], indicating that the structures of both the anion and the cation are important for cellulose dissolution in SILs. The acetate SIL with the $[DBNEt]^+$ cation with an ethyl side chain showed a very low cellulose solubility in comparison to the acetate SIL with the protonated $[DBNH]^+$ cation. The same $[DBNEt]^+$ cation with the $[DEP]^-$ anion outperformed the protonated [DBNH][OAc]. However, this was not the case with the dimethylphosphate anion and the methyl substituted $[DBNMe]^+$ cation, which despite possessing a very high thermal decomposition temperature (T_{onset}), showed relatively poor cellulose solubility; as low as 5.5 wt%. Six ILs, including two imidazolium-, two DBN- and two DBU-derived with acetate and diethylphosphate anions with the highest maximum cellulose solubility were chosen for further study.

We compared Kamlet-Taft parameters of chosen ILs. These parameters are commonly used to describe the solvation properties of a solvent.[42,43] It is known that the ability of a

Table 2. Kamlet-Taft polarity (π*), acidity (α), basicity (β) and "net basicity" (β-α) for the selected ILs.

solvent to dissolve cellulose can be correlated to the solvent basicity (β)[44] and its relation to the solvent acidity – "net basicity" (β-α). Table 2 summarises the Kamlet-Taft parameters for the selected ILs.

Ionic liquid	π*	α	β	β-α
$[C_2C_1im][OAc]$	1.01	0.49	1.09	0.60
$[C_2C_1im][DEP]$	1.37	0.19	1.03	0.85
[DBUEt][DEP]	1.91	0.54	1.17	0.64
[DBUH][OAc]	1.77	0.56	1.05	0.48
[DBNH][OAc]	1.01	0.62	1.17	0.55
[DBNEt][DEP]	1.85	0.65	1.11	0.45
[DBNEt][OAc]	1.35	0.42	1.19	0.77

We compared these parameters with those of [DBNEt][OAc], a poor cellulose solvent. Experimentally it has been found that to dissolve cellulose, ILs require β-values above 0.80 and "net basicity" in the range 0.35-0.90.[43] As can be seen from Table 2, that all of our ILs chosen for further study satisfy these requirements. However, [DBNEt][OAc], analysed here for comparison showed β = 1.19. This could misleadingly suggest that there may be an upper limit to the basicity required for a good cellulose solvent, which is lower than 1.19.

However, another good cellulose solvent $[C_4C_1im][OAc]$ has a β = 1.20[43] and only solvents with higher basicities such as 1.28 and 1.34 as for tributylphosphonium and trihexilphosphonium dimethylphosphates ($[P_{444}][DMP]$ and $[P_{666}][DMP]$), respectively, are considered as explicitly non-solvents for cellulose.[43]

Parviainen et al. have used Kamlet-Taft parameters to predict cellulose solubility in a range of other SILs. Their work concluded that [DBNH][Prop] and [TMGH][Prop] which have Kamlet-Taft parameters close to those of [DBNH][OAc] reported here, to be the most promising SIL for cellulose dissolution.[37]

Viscosity of ILs and cellulose solutions

Among the six selected ILs with high cellulose solubility all, apart from [DBNH][OAc] and [DBUH][OAc] are liquids at room temperature; however their viscosities are very different. The viscosity of the spinning solution is one of the most important factors for fibre processing. The viscosity of the cellulose solutions increases with an increased cellulose concentration. However the viscosity of an IL has no correlation to its dissolution capability, but rather to the speed of cellulose dissolution.[37]

Fig. 2. shows the dependence of solution viscosity on the cellulose content at the temperature of spinning, 80 °C. At a high cellulose content the $[C_2C_1im][OAc]$ solution remained less viscous, while the [DBNH][OAc] solution showed the highest viscosity. Diethyl phosphate ILs solutions up to 10 wt% of cellulose possessed viscosities values very close to those for $[C_2C_1im][OAc]$ solutions, but their viscosities increase at higher concentrations.

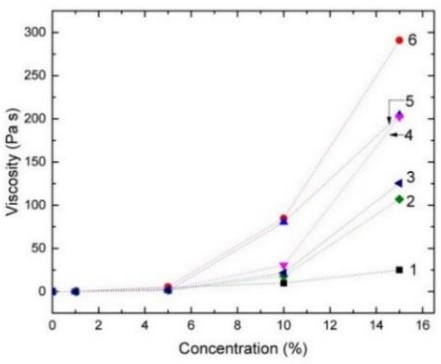

Fig. 2 Viscosities of cellulose solutions in selected ILs at 80 °C: 1) $[C_2C_1im][OAc]$, 2) [DBUEt][DEP], 3) $[C_2C_1im][DEP]$, 4)[DBNEt][DEP], 5) [DBUH][OAc], 6)[DBNH][OAc].

Thermal stability of ILs and cellulose solutions

T_{onset} values collected in Table 1 give the first approximation of the thermal stability of ILs, but tend to overestimate their long-term thermal stability. Therefore, the $T_{0.01/10}$ already reported for $[C_2C_1im][OAc]$, and found to be 102 °C,[45] was also calculated for $[C_2C_1im][DEP]$ and the SILs. The $T_{0.01/10}$ parameter corresponds to the temperature at which 1% weight loss will occur in 10h. From the data illustrated in Supplementary Information Fig. S1 it was estimated that $T_{0.01/10}$ for [DBNH][OAc] is 38 °C.

Bearing in mind that the melting temperature of [DBNH][OAc] of 61 °C one could conclude that this SIL degrades even when solid at a temperature slightly higher than room temperature. The $t_{0.99}$ vs temperature plots for other ILs are presented in Supplementary Information (Fig. S2) and corresponding $T_{0.01/10}$ values tabulated in Table 3. Our TGA analyses conducted at 80 °C showed that both [DBUEt][DEP] and [DBNEt][DEP] showed good thermal stability, comparable to those of imidazolium based ILs (Fig. S3a). The addition of cellulose generally improves the thermal stability of all studied ILs, apart from [DBUH][OAc] (Fig. S3b). This is possibly due to a specific interactions between cellulose and [DBUH][OAc] resulting in the production of non-stable side products at lower temperatures. Overall, these results mean that the solutions of [DBNH][OAc] and [DBUH][OAc] should not be stored at elevated temperatures or heated for prolonged times when large batches are processed. With regards to cellulose degradation upon dissolution and regeneration our analysis showed that these ILs degraded cellulose to approximately the same level. The original cellulose polymerisation degree (DP_w) was measured as 263 and slightly decreased upon dissolution and precipitation of the cellulose (Table 1, far right column).

Table 3. Temperature of 1% weight loss of IL occurs within 10h ($T_{0.01/10}$).

Ionic liquid	$T_{0.01/10}$, °C
$[C_2C_1im][OAc]$	102[45]
$[C_2C_1im][DEP]$	96
[DBUEt][DEP]	130
[DBUH][OAc]	67
[DBNH][OAc]	38
[DBNEt][DEP]	56

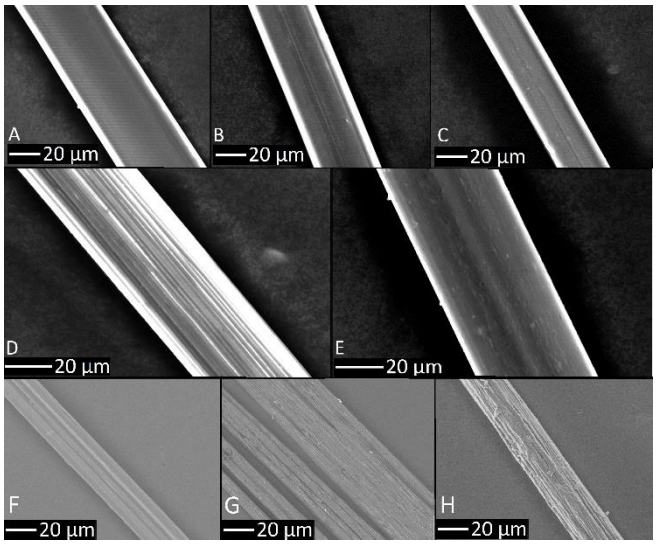

Fig. 3 SEM images for the fibres spun from ILs, A) [DBNET][DEP], B) [C_2C_1im][DEP], C) [DBNH][OAc], D) [DBUET][DEP], E) [C_2C_1im][OAc], F) [DBNH][OAc][Hex], G) [DBUH][OAc], H) [C_2C_1im][OAc][Hex].

Cellulose fibres characterisation

These six ILs ([C_2C_1im][OAc], [C_2C_1im][DEP], [DBUEt][DEP], [DBUH][OAc] and [DBNH][OAc]) were used to produce 4 wt% cellulose spinning solutions, from which fibres were spun.

Additionally, to study the influence of the length of the anion chain of ILs on properties of the produced cellulose fibres, fibres were spun from a mixture of 10 wt% (12.65 mol%) [DBNH][Hex] in [DBNH][OAc] (further abbreviated as [DBNH][Hex][OAc]). The 1:9 ratio between these SILs, one poor and the other a good cellulose solvent, allowed the production of a stable spinning solution.

The fibres' diameters were measured using SEM. Five samples from each fibre were tested at five different sections and the mean measured value was taken to calculate the mean cross-sectional area, assuming a circular cross section. Fig. 3 shows SEM images of the fibres' cross sections. The mean values of the diameters measured are given in Table 4.

A slight variation in the diameters of the fibres was observed. It was found that the cellulose fibres spun from [DBUH][OAc] were not completely consolidated after coagulation and were merged/fused with each other during winding. This made it difficult to separate a single filament and measure an individual fibre diameter. Hence, mechanical testing was not performed on these fibres. It is clear from Table 4 and Fig. 4 that fibres spun from [C_2C_1im][DEP] possess the highest Young's modulus of 20 (±2.3) GPa and a tensile strength of 281.5 (±30.5) MPa.

The replacement of an acetate anion with a diethyl phosphate anion for the DBN derived SIL resulted in a slight increase in both Young's modulus and tensile strength of the produced fibres.

Interestingly, the addition of [DBNH][Hex] to [DBNH][OAc], resulting in [DBNH][OAc][Hex], significantly improved the tensile modulus (from 4.6 to 14.4 GPa) and the tensile strength (from 78.9 to 209.9 MPa) of the obtained fibres. The obtained tensile modulus is comparable to 15 GPa previously reported for viscose fibres.[46]

Table 4. Mechanical properties of the produced fibres. Values in brackets are standard deviations from the mean.

IL	Young's Modulus (GPa)	Tensile Strength (MPa)	Diameter (µm)
[C_2C_1im][OAc]	14.9 (±5.3)	250 (±50.3)	51.3 (±2.8)
[C_2C_1im][DEP]	20 (±2.3)	281.5 (±30.5)	24.4 (±1.2)
[DBNEt][DEP]	7.5 (±1.4)	97.3 (±21.6)	45.8 (±2.1)
[DBUEt][DEP]	5.3 (±0.8)	81 (±8.5)	39.9 (±1.5)
[DBNH][OAc]	4.6 (±1.1)	78.9 (±9.0)	38.3 (±1.2)
[DBNH][OAc][Hex]	14.4 (±1.8)	209.9 (±26.1)	28.8 (±2.3)
[C_2C_1im][OAc][Hex]	5.6 (±0.6)	80.2 (±7.2)	38.1(±3.0)

Perhaps in this IL mixture, the $[OAc]^-$ anion is responsible for the dissolution of cellulose, while long chain $[Hex]^-$ affects the alignment of the cellulose chains. Fibres produced from the mixture of SILs are the most promising for textile applications among all SIL-based fibres studied in this work. To investigate this effect of elongation of the anion chain length on imidazolium based ILs, we blended [C_2C_1im][Hex] and [C_2C_1im][OAc] in the same ratio of 1:9 to produce [C_2C_1im][Hex][OAc]. Surprisingly, the mechanical properties of the cellulose fibres produced from [C_2C_1im][Hex][OAc] were poorer when compared to the ones produced from pure [C_2C_1im][OAc] solution and the blended fibre structure was the roughest among all studied fibres (Fig. 3). These blended fibres showed the smallest Young's modulus and tensile strength among fibres obtained from imidazolium-based ILs (Table 4). While the obtained values for [C_2C_1im][OAc][Hex] were comparable to those for other SILs, [DBNH][OAc][Hex] has clearly outperformed the imidazolium-based blend. Perhaps imidazolium cation, known to affect cellulose dissolution via hydrogen bonding interactions,[47–49] interfere with the $[Hex]^-$ anion alignment of the cellulose chains.

From Fig. 4 it can be seen that the fibres spun from [C_2C_1im][DEP], [C_2C_1im][OAc] and [DBNH][OAc][Hex] exhibit a good combination of strength, stiffness and relatively high

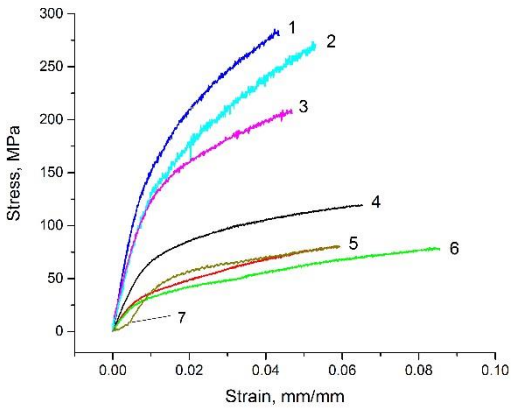

Fig. 4 Stress-Strain curve for the cellulose fibres spun using various ionic liquids representing the tensile strength and the strain at failure for each source of the fibres: 1) [C_2C_1im][DEP], 2) [C_2C_1im][OAc], 3) [DBNH][OAc][Hex], 4) [DBNET][DEP], 5) [DBNH][OAc], 6) [DBUET][DEP], 7)[C_2C_1im][OAc][Hex].

strain to failure. These properties are together attractive for applications in textiles and fibre reinforcement in renewable composites. However, the known reactivity of [C_2C_1im][OAc] with cellulose has prevented this ionic liquid from giving commercially spinnable fibres.[24] Our studies confirmed a reactivity similar to [C_2C_1im][OAc] for [C_2C_1im][Hex] and [C_2C_1im][DEP] (but not DBN- or DBU-based ILs) towards cellulose (Supplementary Information, Fig. S3). Therefore, the fibres produced from [DBNH][OAc][Hex] are of most interest for future exploration in cellulose fibre processing.

Carbonisation of cellulose fibres

All studied fibres were subjected to pyrolysis to produce carbon filaments. We employed Raman spectroscopy as a useful tool to characterise the microstructure of carbon fibres. As shown in Fig. 5, two characteristic bands were observed, which are the D-band located at ~1340 cm^{-1} and the G-band located at ~1590 cm^{-1}. The intensity ratio between the D and G bands (ID/IG) is widely used to give information on the structure and crystallinity of different forms of carbon materials

The intensity ratio between the D and G bands (I_D/I_G) is widely used to give information on the structure and crystallinity of different forms of carbon materials.[50] The G band arises from an in-plane bond stretching motion of sp^2-hybridized carbon atoms and the D band is related to the breathing mode of the aromatic ring near the basal edge.[51] The third main characteristic band at ~2700 cm^{-1} (*G'* or 2*D* band) was not observed for any of the fibres due to the absence of a highly graphitic structure, which typically starts to evolve at temperatures above 1200 °C.[18] The D band can be correlated to structural disorder in the fibres. This D band only appears in the presence of disorder in carbon fibres.[52]

As shown in Table 5, the I_D/I_G ratios for all carbon fibres are consistent with the values observed for other carbon fibres carbonised from regenerated cellulose filaments.[18,19] Carbon fibres produced from cellulose solutions in [C_2C_1im][OAc][Hex] and [DBNH][OAc][Hex] exhibit slightly lower I_D/I_G ratios than other fibres that may correspond to the formation of more crystalline structures.[18,19]

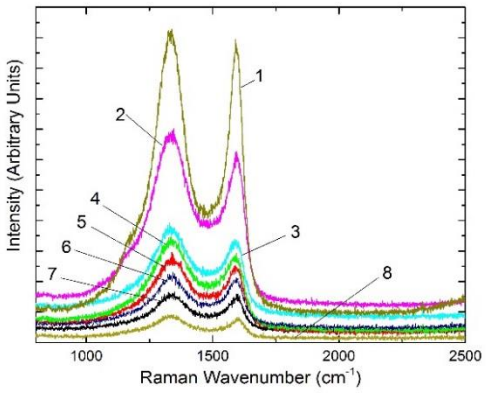

Fig. 5 Typical Raman spectra of the carbon fibres produced from solutions in ILs : 1) [DBNET][DEP], 2) [DBUET][DEP], 3) [C_2C_1im][OAc], 4)[C_2C_1im][DEP], 5) [DBNH][OAc]/ [DBNH][Hex], 6) [DBUH][OAc], 7) [DBNH][OAc].

Table 5. I_D/I_G ratios and Full Width Half Maxima (FWHM) values of the D and G Raman bands.

IL	I_D/I_G	FWHM-D band	FWHM-G band
[C_2C_1im][OAc]	1.17	231	76
[C_2C_1im][DEP]	1.10	210	69
[DBNH][OAc]	1.13	187	61
[DBUH][OAc]	1.05	191	71
[DBUEt][DEP]	1.08	229	75
[DBNEt][DEP]	1.13	206	77
[DBNH][OAc][Hex]	1.02	188	73
[C_2C_1im][OAc][Hex]	1.04	172	67

The full width half maximum (FWHM) values of both peaks are also tabulated in Table 5 and these values provide information on crystallinity and ordering. The carbon fibres derived from [C_2C_1im][OAc][Hex] exhibit slightly sharper and narrower D and G peaks indicating higher crystallinity and structural order than the rest of the fibres.

The low I_D/I_G ratio, indicates a higher G peak intensity corresponding to the formation of more structurally ordered fibres; this decreases according to the trend:

[C_2C_1im][OAc] > [DBNH][OAc] ≈ [DBNEt][DEP] > [C_2C_1im][DEP] > [DBUEt][DEP] > [DBUH][OAc] > [C_2C_1im][OAc][Hex] > [DBNH][OAc][Hex].

Further work would be required to obtain fibres at higher temperatures (>1200 °C) to follow the complete graphitization of these materials.

Conclusions

In this work we determined that SILs derived from DBU and DBN with acetate and diethyl phosphate anions were promising cellulose solvents, reaching cellulose solubilities as high as their imidazolium analogues. Based on the maximum cellulose solubility and thermal properties of these ILs, we have determined six ILs as promising solvents for cellulose processing: [C_2C_1im][OAc], [C_2C_1im][DEP], [DBUEt][DEP], [DBUH][OAc] and [DBNH][OAc]. Their performance was explained by Kamlet-Taft values. The relatively high basicity of [DBNEt][OAc] (β = 1.19) could be a reason for its poor cellulose dissolution ability in comparison to other acetate SILs based on this superbase ([DBNH][OAc] and [DBNEt][DEP]). At a high cellulose content the [C_2C_1im][OAc] solution remained less viscous in comparison to the other ILs. [DBUEt][DEP] showed viscosity of cellulose solutions similar to [C_2C_1im][OAc] at moderate concentrations, and possessed higher thermal stability; however the cellulose fibres produced from [DBUEt][DEP] were of low quality and merged with each other. It was found that the elongation of the carboxylic chain of the anion led to a decreased cellulose dissolution ability. However, the introduction of 10 wt% of the hexenoate SIL to [DBNH][OAc] resulted in stronger fibres and carbon fibres with a higher order. Overall, fibres spun from the [DBNH][OAc][Hex] mixture have mechanical properties similar to those obtained

from $[C_2C_1im][OAc]$ and produce higher structurally ordered fibres when carbonised. We hypothesise that the introduction of hexanoate anion assists the alignment of the cellulose chains and therefore produced fibres possessing higher mechanical properties. This principle did not work with the imidazolium analogue $[C_2C_1im][OAc][Hex]$. Cellulose fibres produced from the solution in $[C_2C_1im][OAc][Hex]$ had a rough surface and moderate mechanical properties. These fibres when carbonised however gave highly ordered carbon fibers with the second highest I_D/I_G value for the fibres studied in this work.

Therefore here we determined certain similarities and differences in the performance of imidazolium and superbase based ILs for cellulose processing into textile fibres and carbon fibres and defined [DBNH][OAc][Hex] as the most promising cellulose solvent among those studied here.

Experimental section

Materials. Cellulose was purchased from Sigma-Aldrich. Ionic liquids were synthesised by acid-base neutralisation from corresponding bases and acids. The procedure is described in detail in the Supplementary Information.

Thermogravimetric Analysis (TGA) experiments were performed on a PerkinElmer 'Pyris 1 TGA' analyser in the range 30 – 500 ^{o}C with a ramping rate of 10 ^{o}C min^{-1} and a nitrogen flow of 20 ml min^{-1}.

Maximum cellulose solubility was determined by combining the IL and an excess of pulp, stirring the mixture with an overhead stirrer at 80 °C for 4 hours, followed by centrifugation of undissolved cellulose pulp. The homogeneous top phase obtained after centrifugation was weighed and the cellulose extracted with ethanol and dried. The ratio of the mass of the obtained dry cellulose to the mass of its homogeneous solution gives the maximum cellulose solubility in this IL. Obtained solutions however, were in a form of a very high viscous gel, and therefore much lower concentrations were prepared for further analysis and spinning.

Cellulose was dissolved at 80 °C using a hotplate and an oil bath. Stirring was performed using a mechanical overhead stirrer. Homogeneity of the solutions was confirmed using optical microscopy.

Polymerisation degree (DP_w) of cellulose was measured for neat cellulose and cellulose recovered from its 10 wt% solution in ionic liquid by Gel Permeation Chromatography (GPC) in a lithium chloride/dimethylacetamide (LiCl/DMA) organic mobile phase, as described by Potthast *et al.*[53]

Kamlet–Taft parameters (α, β and π*) were measured with the application of the solvatochromic dyes: (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye 33, from Fluka), 4-nitroaniline (from Sigma-Aldrich), and N,N-diethyl-4-nitroaniline (from Sigma-Aldrich). Stock solutions of each dye in dichloromethane (DCM) were prepared. Equal volumes of the stock solutions were combined with ionic liquid, then the DCM was evaporated. The dye concentration was chosen to produce spectra with an absorbance between 0.10 and 0.25. UV-Vis measurements were carried out in quartz cuvettes with a 10 mm path length at 25 °C. The Kamlet–Taft parameters were calculated from the absorption maxima as described in the literature.[54]

Viscosity measurements were performed on a TA instruments 'AR2000ex' rheometer fitted with a Peltier plate at 25 °C, using a 40 mm, 2° steel cone. Measurements were performed at an angular velocity between 0.1 and 10 rad s^{-1} under a nitrogen atmosphere.

Spinning solutions were prepared upon dissolution of 4 wt% of cellulose pulp in the ILs for 4h at 80 °C with a consequent degassing of the obtained solutions for 2h in vacuum oven at 80 °C.

Cellulose fibres were spun at 200 rpm using a 340 mm diameter needle with a 2 mL min^{-1} extrusion rate. Wet extrusion was performed with a Nexus 6000 syringe Pump, with a draw ratio of 6. Water was used as coagulation bath and an air gap of 3 mm was used between the water bath and the needle. The fibres were kept in water to remove the residual ionic liquid for two days and were left to dry at room temperature for another two days.

The fibres' diameters were measured using a SEM-TM3030 Plus Table Microscope with a Deben Sprite Multi Axis Stage Controller. Five samples from each fibre were tested from five different circular cross-sections to measure the diameter, and the mean value was taken to calculate the cross-sectional area of the fibres.

The tensile strength of the fibres was tested using a single fibre testing machine from Dia-Stron Ltd. A 20N load cell was used with a stretch rate of 2 mm min^{-1}. The gauge length was set as 2 cm. Stress-strain curves were obtained from this single fibre test for 10 samples from each fibre type. The mean cross-sectional areas for each type of cellulose fibre calculated from the mean diameter readings obtained from SEM testing were used to calculate the tensile strength of the fibres. The Young's modulus were taken from the most linear portion of the stress-strain curves.

As the first step of the carbonisation procedure, stabilisation of the precursor is required for decomposition and rearrangement of the polymer in an oxidative atmosphere. Tang and Bacon[14,15] have shown that thermogravimetric analysis (TGA) of cellulose fibres performed in air exhibited significant pyrolytic degradation initiating at 240 °C. Therefore, stabilization of our fibres was carried out at this temperature. An Elite horizontal tube furnace (TSH16/50/180) was used for both stabilisation and carbonisation. The cellulose fibres were placed in a ceramic boat and inserted into the tube. These fibres were initially stabilized by heating to 240 °C in air at a rate of 5 °C min-1, followed by a 30 min isotherm at the final maximum temperature. As the next step of the process, these stabilised fibres were then carbonised by heating to 1000 °C in an Argon atmosphere at a rate of 10 °C min^{-1}, followed by a 60 min isotherm at the final maximum temperature.

Raman spectra of carbonised fibres were obtained using a Renishaw 1000 Raman imaging microscope equipped with a thermoelectrically cooled CCD detector. A laser with a wavelength of 532 nm was used to record spectra from fibres

using an exposure time of 10 s and two accumulations. The laser intensity was reduced to 10 % and the beam was focused using a x50 objective lens onto one or a few carbon fibres.

Conflicts of interest

There are no conflicts of interest to declare.

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